REFRACTORIES FOR GLASS PRODUCTION

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CORROSION RESISTANCE OF REFRACTORIES MADE FROM LOW-CEMENT CONCRETES FOR GLASS MAKING

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The corrosion resistance of samples made of low-cement concrete to a bottle glass melt was investigated in dynamic conditions at a temperature of 1350°C; they are used for production of articles used in glass-forming machines.

The domestic refractory industry does not fully satisfy the needs of the glass industry with respect to the assortment and quality of most of the refractories manufactured for glass-melting furnaces [1 – 3]. For this reason, glass works use furnaces in conditions of lower (sometimes by 1.5 – 2 times) output of glass melt from the melting area or to increase output, purchase foreign high-quality refractories which are several times more expensive than the domestic analogs, which affects the cost of the products manufactured.

The quality of the refractories in direct contact with the working media in the glass-melting furnace (roof, walls, bottom of the melting part, etc.) plays an important role in ensuring high-quality glass products. In addition to the refractories in the melting zone, the articles in the production part (feeder elements and glass-forming machines), which have a complex configuration with elevated requirements both with respect to performance characteristics and with respect to shape and size as a function of the application, have a large effect on quality. During their lifetime, refractories are exposed to the intensive effect of the glass melt and important thermal and mechanical stresses, so that they must have high glass and thermal stability, strength, and must also provide for constant assigned parameters of feed of the glass melt for processing and its temperature homogeneity [4].

The production channel or feeder channel directly adjacent to the working part of the tank is designed for feeding glass melt to the feeder and then processing it by the glass-forming machine. The temperature of the glass melt in the feeder channel is 1000 – 1350°C as a function of the type of glass. The concrete temperature is established to ensure a uniform decrease in it to the level determined by the viscosity of the glass melt required for forming. Defects in the form of stone, ripples, and seeds that enter with the glass melt and appear in reaction of the glass melt with the refractory lining cannot be assimilated directly in the channel by the glass mass. For this reason, the refractories for lining the feeder channel must satisfy certain requirements; the basic requirement is slow, uniform dissolution in the glass melt without formation of any defects.

Many requirements are imposed on refractories used in glass-melting furnaces; the most important one is corrosion resistance to the glass melt (glass resistance) [5 – 7]. The glass resistance, characterized by the rate of dissolution of a refractory in a glass melt, is a function of many factors: the chemical and mineral compositions and the structural features of the refractory, the chemical composition and viscosity of the glass melt, the surface tension on the boundary of the glass and the refractory, etc.

In the domestic scientific and technical literature, insufficient attention has been focused on studying the glass resistance of the refractories used in the glass industry. The study of the corrosion resistance of molded and electrosmelted refractories used in glass-melting furnaces in most cases dates back to the end of the 1960s, beginning of the 1970s (Table 1) [5, 8 – 11]. The tests were basically performed with a static method which consisted of holding the refractory sample in a glass melt at rest for a fixed time. This method is characterized by accessibility and simplicity of implementation but the long duration of the process and insufficient modeling of the real conditions of service of the refractories are important drawbacks.

When a refractory reacts with a glass melt, a contact layer is formed, characterized by much higher viscosity in

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TABLE 1

Refractory	Glass resistance determined by the static method, mm/day	Testing temperature, °C
Sodium-calcium-silicate glass		
Molten quartz	9.90	1500
Dinas	12.00	1500
Chamotte (26 – 39% Al_2O_3)	2.03 – 3.50	1400
Kaolin (40 – 42% Al_2O_3)	1.65	1400
High-alumina (68 – 72% Al_2O_3)	1.11	1400
Baddeleyite–corundum*	0.96 – 1.35	1550
Corundum with B_2O_3 additive	1.30 – 2.65	1400
Borosilicate glass		
Chamotte (30 – 58% Al_2O_3)	2.36 – 2.41	1300
Kaolin (40 – 42% Al_2O_3)	0.95 – 1.94	1300
High-alumina (64 – 72% Al_2O_3)	0.88 – 1.15	1300
Corundum with B_2O_3 additive	1.10 – 1.15	1450
Lead–silicate glass		
Chamotte (30 – 58% Al_2O_3)	1.86	1300
Kaolin (40 – 42% Al_2O_3)	1.58	1300
High-alumina (64 – 72% Al_2O_3)	0.68 – 1.04	1300
Corundum with B_2O_3 additive	0.20 – 0.50	1450

* The glass resistance of baddeleyite–corundum refractory, determined by the dynamic method, was 15.7 – 28.4% at a testing temperature of 1550°C.

comparison to the viscosity of the glass melt. One of the drawbacks of the static method is that the viscous intermediate layer persists for a long time, preventing further penetration of the melt into the refractory. In real conditions in glass-melting furnaces, the glass melt is in constant motion, washing off the products of the reaction of the glass melt with the refractory. For this reason, a dynamic method is preferable, based on rotation of the refractory sample in the glass melt at a fixed rate so that real modeling of the character of the effect of the glass on the refractory in industrial conditions takes place.

Refractories made of low-cement, ultralow-cement, and zero-cement concretes, which have a number of advantages in comparison to traditional molded refractories, have recently been relatively widely used in the metallurgical industry [12 – 14]. These materials are also promising for the glass industry, where they are still only used for lining glass-melting furnace parts.

Semiluki Refractory Works Co. was one of the first Russian refractory enterprises to master the technology for production of articles made of low-cement concrete [15]. Beginning in 2003, the company supplied refractory feeder parts to a number of glass works — low-cement concrete articles of corundum and aluminosilicate compositions, which are currently undergoing certification. In addition to these technologies, new compositions are being developed by the company and the line of refractory concrete articles is being expanded. Assessing the glass resistance of refractories for use in contact with the glass melt is very important for moving new products onto the market. Until recently, there were no data

TABLE 2

Refractory*	Corrosion resistance			
	%/6 h	mm/6 h	%/day	mm/day
VMKS-85	6.4	0.67	25.7	2.69
VShS-40	5.9	0.61	23.7	2.44
VKS-95	1.1	0.12	4.4	0.47
VKTsS	1.5	0.16	6.0	0.63
VMLS-65	2.3	0.24	8.9	0.94
VShS	2.6	0.28	10.5	1.13
VMKS-75	2.2	0.23	8.9	0.93
VMKRS-50	4.0	0.43	16.2	1.72

* VMKS) mullite–corundum composition; VShS) chamotte composition; VKS) corundum composition; VKTsS) mullite–corundum composition with added zircon dioxide; VMLS) mullite composition; VMKRS) mullite–silica composition.

on the glass resistance of materials made of low-cement concretes based on testing for glass resistance.

Corrosion resistance tests were conducted in dynamic conditions on samples of refractory low-cement concretes manufactured by Semiluksk Refractory Works at B. G. Shukhov Belgorod State Technological University. Samples in the form of bars measuring $20 \times 20 \times 250$ mm in a sodium-calcium-silicate glass melt used for manufacturing glass bottles were tested at 1350°C using a special high-temperature setup.

Two transverse notches in the form of grooves from 0.5 to 1.0 mm deep at a distance of 215 and 245 mm from the upper end were made on one face of the sample with a diamond cutting disk. The distance between the notches and the thickness of the sample at the level of the notches were measured with ShTs-I-250-0.05 sliding calipers with an accuracy of ± 0.05 mm. A high-temperature furnace with silicon-carbide heaters was used to perform the tests. A high-alumina (72 – 75% Al_2O_3) crucible manufactured with ceramic-concrete technology [13] containing bottle glass cullet were placed in the furnace. The furnace was heated to 1350°C at the rate of 200 K/h. The temperature was monitored with a platinum thermoelectric transducer. The duration of the tests was 6 h. The glass resistance was expressed in percentage of the change in the volume of the part of the sample between the disks after a certain time and the decrease in its thickness (mm) after the same time, calculated according to OST 3-4230–78.

The results of studying the corrosion resistance of samples made from experimental compositions of low-cement refractory concretes developed at Semiluki Refractory Works are reported in Table 2. Figure 1 shows an overall view of the samples after testing for glass resistance.

The highest glass resistance was characteristic of concretes based on corundum (VKS-95) and corundum with zirconia–mullite additive (VKTsS). The corundum–mullite and mullite compositions (VMKS-75, VMLS-65, and VShS) were less resistant. The lowest corrosion resistance was ob-

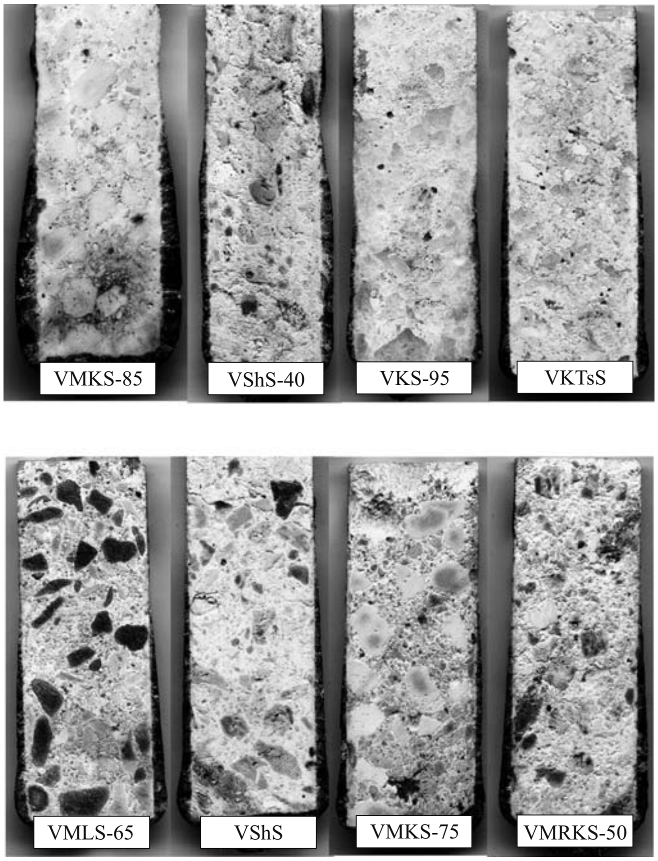

Fig. 1. View of samples after testing for glass resistance in dynamic conditions.

served in the concretes containing an important amount of free silica (VMKS-85, VShS-40, and VMKRS-50).

The phase composition of the contact zones was determined by x-ray phase analysis to study the mechanism of the reaction of these refractories with the glass melt.

In using concrete of corundum composition (Fig. 2*a*, curve *1*), minimal dissolution of the basic component (see Fig. 2*a*, curve *2* and Table 2) takes place, perhaps with formation of feldspar (d/n = 3.26, 3.20, 3.18, and 3.02 Å) and mullite (weak reflection, 5.5 Å). When zirconia–mullite was added to corundum concrete (Fig. 2*b*, curve *1*), mullite primarily dissolved intensively (d/n = 3.43, 3.39 Å) and zirconium dioxide dissolved to a much smaller degree (d/n = 3.18, 2.85 Å) and corundum was almost without formation of new phases (see Fig. 2*b*, curve *2*).

The samples based on VMKS-75 concrete were characterized by an important corundum content (Fig. 3*a*, curve *1*) and a low amount of mullite, which dissolved significantly in comparison to corundum as a result of contact with the glass melt (see Fig. 3*a*, curve *2*). In reacting with the glass melt, the intensity of the corundum reflections increases significantly (see Fig. 3*b*, curve *2*) due to significant dissolution of mullite. In contrast to concretes VMKS-75 and VMLS-65, an important amount of free silica in the form of cristobalite (d/n = 4.12 Å) is observed together with corundum and mullite in the phase composition of the samples of VShS concrete (Fig. 3*c*, curve *1*), which negatively affects the glass resistance of the material. The alkaline components of the glass melt with cristobalite react in the contact zone (see Fig. 3*c*, curve *2*). Partial dissolution with conversion to the amorphous phase is the result of this, and it increases the degree of corrosion since the viscosity of this phase is comparable to the viscosity of the melt so that it is intensively washed out of the contact layer. It should also be noted that an insignificant amount of feldspars is observed in the phase composition of the initial refractory for concretes VMKS-75, MLS-65, and VShS. They are formed as a result of reacting with the CaO contained in high-alumina cement, Al_2O_3, and free silica.

The materials made from concrete VMKRS-50 have mullite–silica composition with a large amount of free silica in the form of cristobalite (Fig. 4*a*, curve *1*). In reacting with the glass melt, the cristobalite and mullite dissolve intensively, as the decrease in the intensity of their reflections in

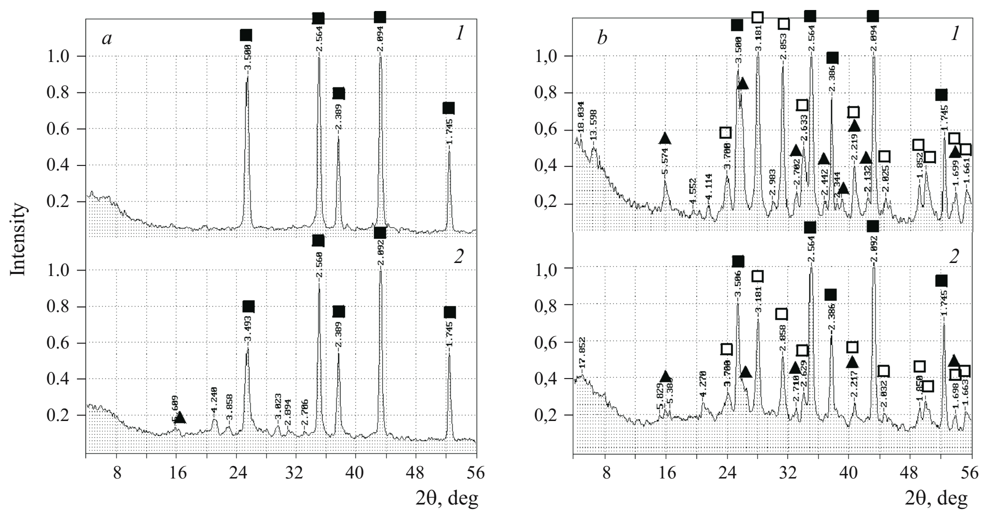

Fig. 2. X-ray patterns of the initial refractory (*1*) and the contact layer (*2*) of samples based on concretes VKS-95 (*a*) and VKTsS (*b*) after testing for glass resistance: ■) corundum; ▲) mullite; □) zirconium dioxide.

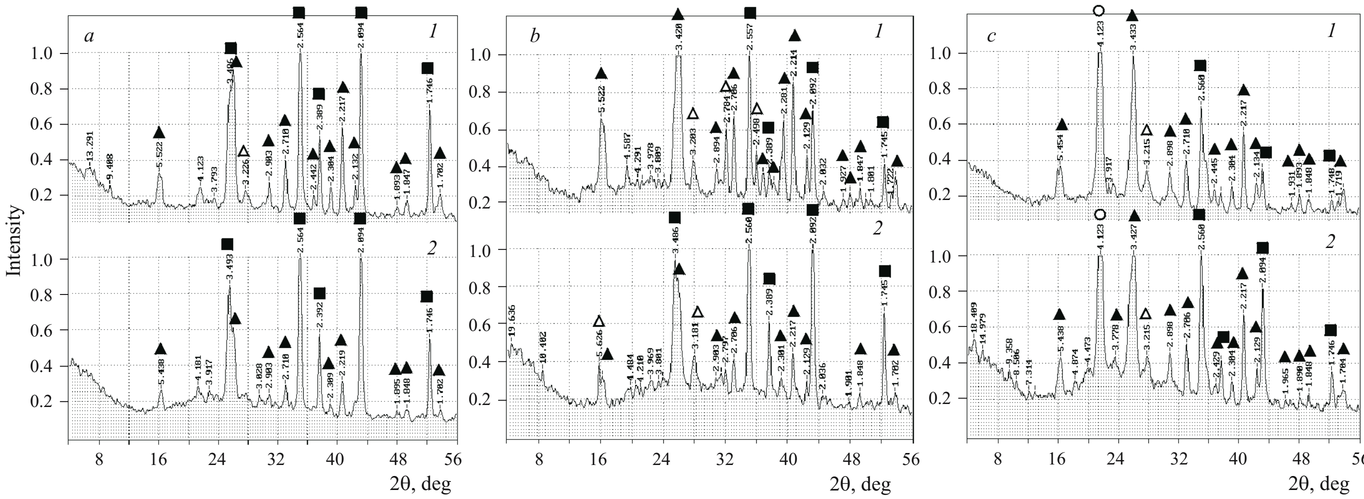

Fig. 3. X-ray patterns of the initial refractory (*1*) and contact layer (*2*) of samples of VMKS-75 (*a*), VMLS-65 (*b*), and VShS-2 (*c*) concretes after testing for glass resistance: ■) corundum; ▲) mullite; △) feldspar; ○) cristobalite.

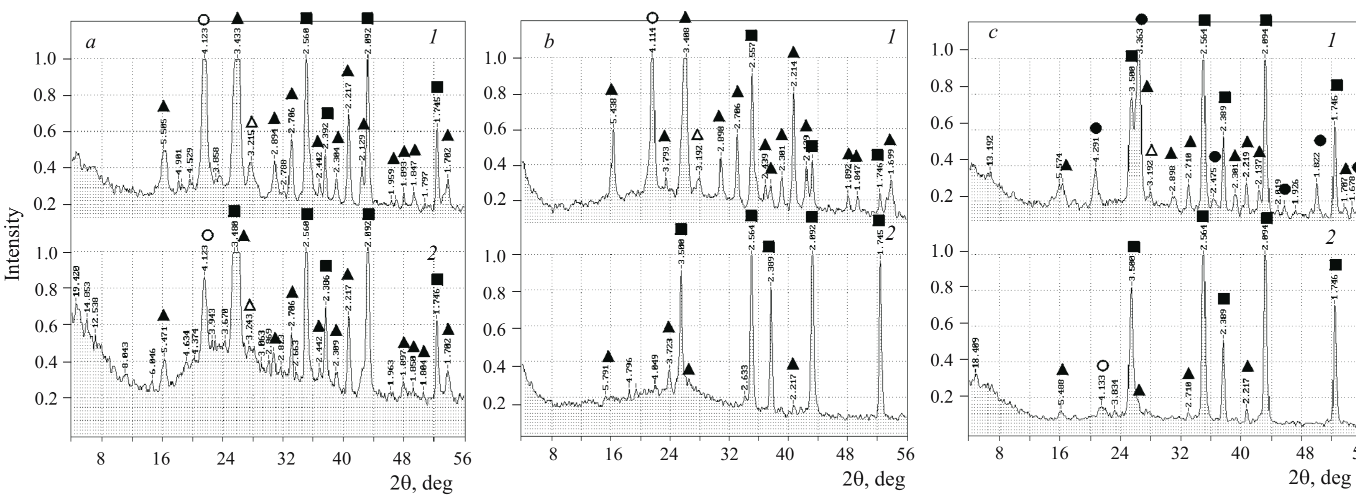

Fig. 4. X-ray patterns of the initial refractory (*1*) and contact layer (*2*) of samples of VMKRS-50 (*a*), VShS-40 (*b*), and VMKS-85 (*c*) concrete after testing for glass resistance: ■) corundum; ▲) mullite; △) feldspar; ○) cristobalite; ●) quartz.

the x-ray pattern indicates (see Fig. 4*a*, curve *2*) and an important increase in the amount of amorphous phase is also observed. In contrast to the VMKRS-50 materials, cristobalite and corundum content is lower in the samples based on VShS-40 concrete (Fig. 4*b*, curve *1*). In contact with the glass melt, the cristobalite and mullite almost totally dissolve, and corundum remains the predominant phase (see Fig. 4*b*, curve *2*). A distinctive feature of concrete VMKS-85 is the presence of free quartz (d/n = 4.29, 3.36 Å) in the predominantly corundum phase (Fig. 4*c*, curve *1*); in reacting with the glass melt, it almost totally dissolves with formation of an insignificant amount of cristobalite (see Fig. 4*c*, curve *2*).

Low-cement refractory concretes of corundum and corundum–zirconia composition (VKS-95, VKTsS) are thus the most resistant to bottle glass melt. Low-melting compounds (feldspar) are not formed in the contact zone in use of these refractories, and this causes their slow dissolution in the glass melt. The use of such refractories allows extending the time between repairs and increases the efficiency of operation of glass-forming machines.

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